Renewable Energy 160 (2020) 919–930

Contents lists available at ScienceDirect

Renewable Energy

journal homepage: www.elsevier.com/locate/renene

Hydrogenolysis of glycerol to 1,2-propanediol without external H_2 addition in alkaline medium using Ni-Cu catalysts supported on Y zeolite

Taynara S. de Andrade , Mariana M.V.M. Souza , Robinson L. Manfro *

Escola de Química, Universidade Federal do Rio de Janeiro - UFRJ, Centro de Tecnologia, Bloco E, sala 206, CEP 21941-909, Rio de Janeiro, RJ, Brazil

ARTICLE INFO

Article history:
Received 15 April 2020
Received in revised form
6 June 2020
Accepted 12 June 2020
Available online 22 June 2020

Keywords:
1,2-Propanediol
Hydrogenolysis
Glycerol
Nickel—copper

ABSTRACT

Ni, Cu and Ni-Cu catalysts supported on NaY-zeolite (NaY) were prepared with 20 wt% of each metal by using wet impregnation method. They were characterized by X-ray fluorescence, X-ray diffraction, N_2 adsorption-desorption, temperature-programmed reduction, temperature-programmed desorption of ammonia and temperature-programmed oxidation. The catalytic tests of glycerol hydrogenolysis were performed in alkaline medium (NaOH/glycerol molar ratios of 0, 0.25 and 0.5) employing continuous flow reaction system using a space velocity of 2 h^{-1} at 260 °C, and pressure of 46 bar for 30 h. The catalytic tests showed that the concomitant use of Ni and Cu proved to be more effective for the process of glycerol hydrogenolysis to 1,2-propanediol without the external H_2 addition, since each metal plays a distinct role. The catalytic tests showed a significant increase in the yield to 1,2-propanediol with the addition of NaOH to the reaction medium; the highest conversion of glycerol (96.4%) and yield to 1,2-propanediol (31.8%) were obtained employing NaOH/glycerol molar ratio = 0.5 and Ni-Cu catalyst. No catalytic deactivation was observed for 30 h, showing that the catalysts exhibit good catalytic stability and good resistance to coke deposition.

1. Introduction

With the increasing environmental concerns and constant incentives for use of renewable inputs, biodiesel has attracted considerable attention since the past decade as an environmentally friendly and renewable biomass fuel [1]. The main production route of biodiesel is through the transesterification of oils or fats from plants or animals, with short chain alcohol, such as methanol or ethanol, using basic catalysis (commonly, KOH or NaOH) [2]. Glycerol is the main byproduct of this process and it is estimated that to every 90 m^3 of biodiesel 10 m^3 of glycerol are produced [3].

Several researches have been studied a more noble destination for the surplus of produced glycerol, aiming the transformation of glycerol into higher value-added products. Many products may be obtained from glycerol such as 1,3-propanediol, 1,2-propanediol (1,2-PD), β-carotene, propionic acid, epichlorohydrin, ethanol, syngas, and hydrogen [4]. One of the processes studied is hydrogenolysis of glycerol to obtain 1,2-PD. This high value chemical product can be applied in pharmaceutical products, food, cosmetics, paints and animal food, among others [5]. Currently, 1,2-PD is mainly obtained from petroleum-derived propylene via the process involving a selective oxidation of propylene to propylene oxide with its subsequent hydrolysis [6]. The production of 1,2-PD from glycerol hydrogenolysis may be an attractive alternative due to the availability of glycerol in the world market and because it is a sustainable process.

According to the literature, catalysts based on noble metals such as Rh, Pt, Pd, and Ru can be used for glycerol hydrogenolysis [7,8] and, among these catalysts, Ru has proved to be the most active catalyst [9]. However, because of its high cost, many researchers have studied and developed catalysts based on transition metals such as Ni, Cu, Co, Zn, which have a lower cost and have shown promising results [5,10,11]. Among transition metals, copper-based catalysts appears to be highly efficient in hydrogenolysis of glycerol due to their high activity in C-O bond cleavage associated with poor activity for C-C bonds cleavage [12,13].

The hydrogenolysis of glycerol may follow basic route or acid route, depending on the reaction conditions (Scheme 1). By the acid route, glycerol is dehydrated to acetol which is subsequently

* Corresponding author.
E-mail address: robinson@eq.ufrj.br (R.L. Manfro).

https://doi.org/10.1016/j.renene.2020.06.060
0960-1481/